

3 Entropy

It may seem strange that the entropy – which is one of the most subtle concepts of theoretical physics, or natural philosophy – first emerged in the context of an engineering proposition. Namely the question of how to improve the efficiency of heat engines. We shall see how that came about.

Actually the entropy has never shed its hybrid position between physics and engineering: The students of mechanical engineering keep a (temperature-entropy)-diagram among their files, which they are taught to use for the lay-out of power plants and jet nozzles. The chemical engineers are familiar with the *entropy of mixing* which they use to construct phase diagrams, and all physicists know that nature strikes a compromise between entropy and energy when it drives the sap into the tree-tops by osmosis.

Heat Engines

It was Denis Papin (1647–1712) – a student of Christaan Huygens (1629–1695) – who first condensed water and lifted a weight by doing so.¹ Papin owned a long brass tube of diameter 5cm. Some water at the bottom was evaporated, and thus lifted a piston, which was then fixed by a bolt. Afterwards the tube was taken from the fire, the vapor condensed and a Torricelli vacuum formed inside, i.e. a low pressure equal to the vapor pressure appropriate to the extant temperature. When the bolt was removed, the air pressure drove the piston downward and was thus able to lift a weight of sixty pounds. This in a nutshell is the manner in which the *motive power of steam* works: by creating a vacuum through condensation.

Denis Papin knew the properties of saturated vapor well, so that he also knew that water under pressures beyond 1atm boils at a higher temperature than 100°C. He made use of this phenomenon in a pressure cooker: In a closed vessel some tough meat is heated in water. The accumulating steam raises the pressure and thus the boiling point of water, so that the meat finds itself immersed in water as hot as 150°C (say). Thus it becomes sufficiently cooked in a short time. Papin was invited

¹ We shall not enter into speculations about whether and how Hero of Alexandria – in the first century A.D. – employed steam power in the automatic working of doors and statues, which priests used to impose on gullible worshippers, cf. I. Asimov: “Biographies...” loc.cit. p. 38.

to demonstrate his *digester* for the Royal Society of London and he cooked an impressive meal for King Charles II.²

However, Papin's brass tube was not a steam engine yet; it did only one stroke at a time. Proper steam engines were developed later when a pressing need arose in England in the early 18th century. England was suffering a kind of energy crisis: *The country was deforested and what trees remained were needed for the navy and could not be used for fuel.*³ At the same time the output from the coal mines was in decline, and threatened to cease altogether, because of difficulties with drainage at the depth where the pits had arrived. That situation provided a strong incentive for inventors, and so the steam engine came just in time. It was developed by the engineer Thomas Savery (1650–1715) and by Thomas Newcomen (1663–1729), a clever and skilful blacksmith. The machine was at first exclusively used to pump water from mines, so that coal could be brought up from a greater depth, previously inaccessible. Therefore it may not have mattered so much, that a good part of the coal was used to heat the boiler of the engine. Indeed Newcomen's engine was quite wasteful of fuel.⁴

In due time, however, the steam engine was employed by the iron industry to power bellows, and hammers for crushing the ore. Thus coal became a commodity to be paid for by the owners of the iron works, and therefore the efficiency of the engine had to be improved.

The Newcomen machine worked by injection of cold water into the cylinder, cf. Fig. 3.1. Thus the steam was condensed and a good vacuum was developed, which pulled down the piston in a powerful stroke. Afterwards new steam from the boiler pushed the piston back up, before water was injected again, etc.

James Watt (1736–1819) recognized the reason for the wastefulness of the process: A good part of the precious new hot steam condensed while reheating cylinder and piston, which had just been cooled by the injected water. Watt improved the machine by inventing a separate cooler, or condenser, into which the steam was pushed before condensation. The condensed water was then pumped back into the boiler. Watt also introduced other improvements, like

- keeping the cylinder wall warm by heating it with the incoming steam,
- introducing an ingenious system of valves so that the piston could work in both the down-stroke and the up-stroke,

² According to I. Asimov: "Biographies..." loc.cit. p. 204.

³ According to I. Asimov: *ibidem* p. 145.

⁴ Yet the machines were successful. *By 1775 sixty of them had been erected in Cornwall alone and there were about one hundred in the Tyne basin.* According to R.J. Law: "The Steam Engine". A Science Museum booklet. Her Majesty's Stationary Office, London (1965) p. 10.

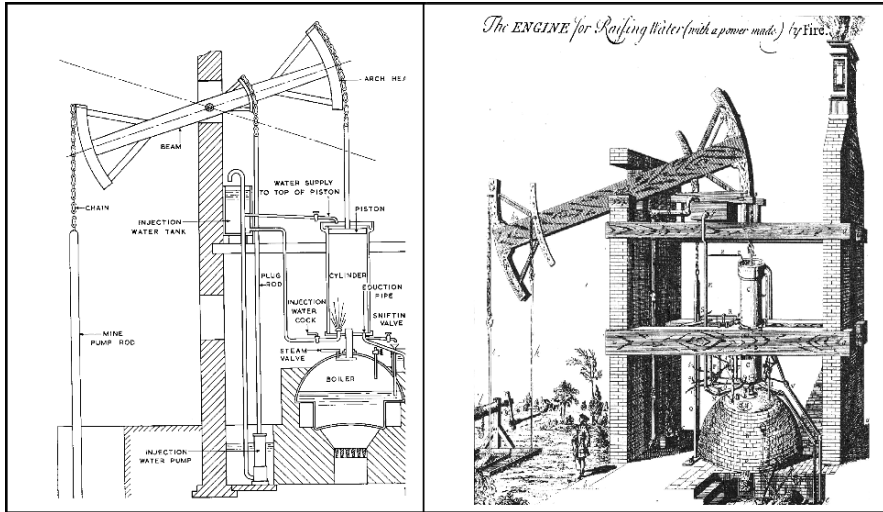


Fig. 3.1. The Newcomen engine

- closing the steam valve before the end of the stroke; it is true that this provided less work per cycle, but it was an efficient measure nevertheless, because still less steam was consumed.

Above all, however, Watt has made the steam engine into more than a pump. He converted the up- and down-movement of the piston into the rotation of a wheel in his famous *rotative engine* with a sun-and-planet transmission gear. This extended the efficacy of the engine greatly, because it could now be used to drive lathes, drills, spinning wheels and looms, – then ships and locomotives. Thus Watt’s machine became the motor of the *industrial revolution*.

James Watt was born in Glasgow. He received an abbreviated education as an instrument maker in London, whereupon he became a laboratory assistant at the University of Glasgow. He repaired and improved a model of the Newcomen machine which had broken down, and was thus able to attract the attention of Joseph Black, the discoverer of the latent heat, see above. Black became Watt’s first mentor and financier, and he introduced him to an industrialist, Dr. John Roebuck, with whom Watt went into a $\frac{1}{3}, \frac{2}{3}$ partnership, – one third for Watt. Later the $\frac{2}{3}$ share was taken over by Matthew Boulton, and the two partners started a successful business selling steam engines. Law writes ⁵ ... *the customer paid for all the materials and found the labour for erection. The firm sent drawings and an erector. They also supplied important parts like the valves and the valve gear...* As

⁵ R.J. Law: “The Steam Engine” loc.cit. p. 13.

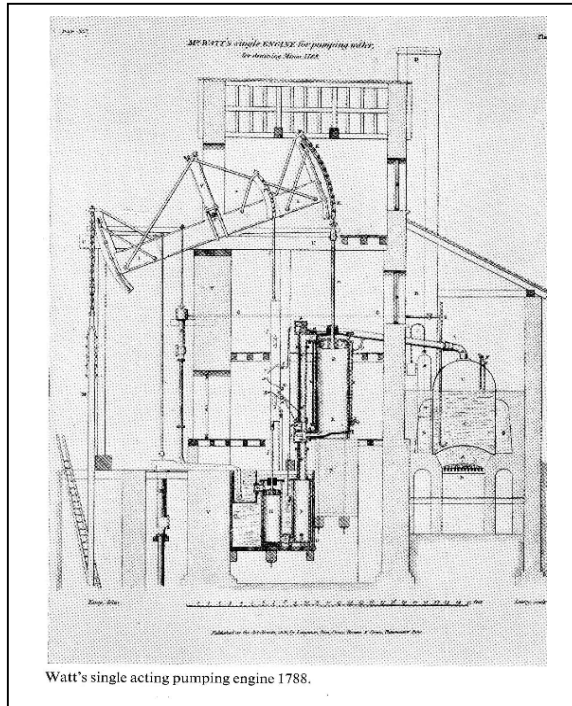


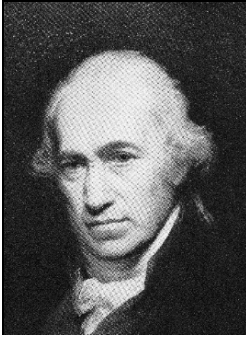
Fig. 3.2. Watt's steam engine

payment, they claimed one third of the saving in coal over the old [Newcomen] engines.

This was enough to make Watt a rich man, because, indeed, Watt's engine was three to four times more efficient than Newcomen's.⁶ Watt retired in 1800. He was famous by then, and much honoured for his life's work. Thus he was elected to membership of the Royal Society of London and he received an honorary doctorate from the University of Glasgow where he had previously served in the lowly position of a laboratory assistant.

Liquid water and steam are particularly well-suited for the conversion of heat into work, because the heat absorbed and emitted – by boiler and cooler respectively – is exchanged isobarically. And a large portion of those isobars are also isotherms, because they lie in the two-phase region of wet steam, where boiling liquid and saturated vapour coexist. This makes the process somewhat similar to a Carnot process, which has maximum efficiency, see below.

⁶ Actually, the efficiencies were all quite low: In Newcomen's case about 2% and 5–7% in Watt's case. A modern power station reaches between 45% and 50%. The engineers have done a good job indeed over the past 200 years.



In 1783 he tested a strong horse and decided that it could raise a 150-pound weight nearly four feet in a second. He therefore defined a “horsepower” as 550 foot-pounds per second. This unit of power is still used, particularly for automobiles. However, the unit of power in the metric system is called 1 Watt, in honour of the Scottish engineer. One horsepower equals 746 Watt.

Fig. 3.3. James Watt. A quote from Asimov⁷

Heat can also be converted into work by an air engine or, more generally, a gas engine. Figure 3.4 shows the prototypical *Joule process* schematically, where an adiabatic compressor furnishes hot air which is then further heated by isobarically absorbing the heat Q_+ . Afterwards the gas cools by adiabatic expansion in the working cylinder which pushes it into a heat exchanger, where it gives off the heat Q_- isobarically. In its alternation between adiabatic and isobaric steps the process is much like the process in the steam engine. However, in the Joule process the isobars are in no way similar to isotherms, since no phase transition occurs.

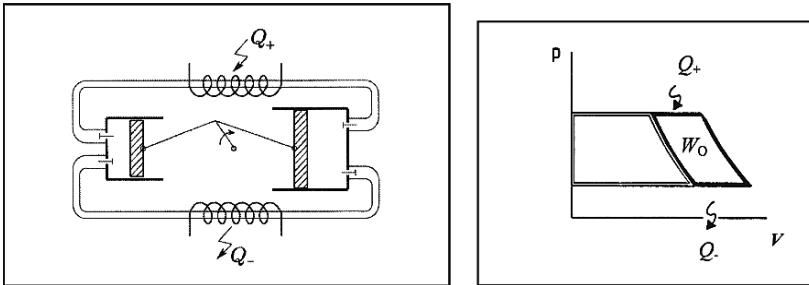


Fig. 3.4. The Joule process and a (pressure, volume)-diagram of the Joule process in an ideal gas

None of the engineers who invented or improved the steam engine – or the air engine – was in any way distracted by any soul-searching about the nature of heat, or whether or not there was a caloric. They proved that heat could produce work *by doing it*, – and doing it better and better as time went on.

The efficiency of the engines climbed up slowly but surely through many ingenious improvement and in the 1820s it had arrived at 18%. At that time

⁷ I. Asimov: “Biographies...” loc.cit. p. 187.

Sadi Carnot, a physicist educated at the École Polytechnique in Paris, posed himself the question, how far this improvement could possibly go and he attempted to find an answer.

Nicolas Léonard Sadi Carnot (1796–1832)

Sadi Carnot was named after the 13th century Persian poet Saadi Musharif ed Din who was *en vogue* in the France of the directorate. His father Lazare Carnot was one of the directors, and later he became one of Napoléon's loyal and efficient generals. The father was also an accomplished mathematician who published a book on mechanical machines in 1803: "Fundamental principles on equilibrium and movement." In that book Lazare Carnot strongly supported the view that a *perpetuum mobile* was impossible.

By hereditary taint, perhaps, the son picked up the question whether the *possible improvements* [of heat engines] *might have an assignable limit*.

And, in 1824, Sadi Carnot published a book in which he addressed the problem: "Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance"⁸ Everything seemed conceivable at the time:

- The process in which heating and cooling occurred at constant pressures might be improved by letting the heat exchange occur at constant volumes or constant temperatures, and
- perhaps working agents like sulphur or mercury might have an advantage over water.

Carnot came to correct conclusions concerning both propositions. About the first one he says:

The best manner to employ a heat engine, whose working agent assumes temperatures between T_{Low} and T_{High} in the process, is *the* engine – which we now call a Carnot engine – which exchanges heat *only* at those temperatures.

Because, so Carnot, [that process is] *...le plus avantageux possible, car il ne s'est fait aucun rétablissement inutile d'équilibre dans la calorique*.⁹

⁸ S. Carnot: [Reflections on the motive power of fire and on machines fitted to develop that power] à Paris chez Bachelier, Libraire. Quai des Augustin, No. 55 (1824). English translation by R.H. Thurston: "Reflections on the motive power of fire by Sadi Carnot and other papers on the second law of thermodynamics by É. Clapeyron and R. Clausius." E. Mendoza (ed.) Dover Publ. New York (1960). pp. 1–59.

⁹ S. Carnot: "Réflexions..." loc.cit. p. 35.

The argument goes like this: Carnot plausibly postulates that a machine is optimal when the temperature of the working agent is always homogeneous and, if it changes in time, that change must be connected with a change in volume.¹⁰ Other changes in temperature are useless, and even detrimental. It is clear that the steam engine does not satisfy that optimality condition, since the cold feed-water from the condenser enters the hot boiler, so that a *rétablissement inutile* must occur. Actually Carnot shows a lot of insight and ingenuity here, because in a lengthy footnote he proposes to preheat the feed-water by condensing a part of the vapour after partial expansion and at a temperature intermediate between boiler and the principal condenser.¹¹ This kind of feed-water preheating – actually in several steps – is done routinely in modern power stations; it is known as *Carnotization* of the steam engine process. To be sure, in order to be practical, the procedure requires expansion in a turbine, not in a steam cylinder, but the principle was recognized by Carnot.

Concerning Carnot's second proposition, – the one on the potential advantage of using an agent other than water – he comes to the conclusion that

When a Carnot engine is used, all agents provide the same work.

In Carnot's words: *La puissance motrice de la chaleur est indépendante des agents mis en oeuvre pour la réaliser ; sa quantité est fixée uniquement par les températures entre lesquels se fait en dernier résultat le transport du calorique.*¹²

This statement is proved by letting two Carnot engines – with different agents, but the same heat exchanges, and in the same temperature range – work against each other, one as a heat engine and one as a refrigerator, or heat pump. If one engine requires more work than the other one produces, we should be able to create *motive power without consumption either of caloric or of any other agent whatever. Such a creation is entirely contrary to ideas now accepted, to the laws of mechanics and of sound physics. It is inadmissible. It would be perpetual motion.*¹³

It was his insight into the working of heat engines that permitted Carnot to come to these conclusions. For the above arguments it was quite irrelevant, whether he knew what heat was, – and he didn't! Indeed, Carnot believed in the caloric theory of heat and he thought that the caloric entering the boiler came out of the cooler *unchanged in amount*. Therefore it was natural for Carnot to draw an analogy between the motive power of heat and that of a waterfall, – *une chute d'eau*, see Fig. 3.5.

¹⁰ S. Carnot: *ibidem* p. 23.

¹¹ S. Carnot: *ibidem* p. 26.

¹² S. Carnot: *ibidem* p. 38.

¹³ S. Carnot: *ibidem* p. 21.



... on peut comparer avec assez de justesse la puissance motrice de la chaleur à celle d'une chute d'eau : toutes deux ont un maximum que l'on ne peut pas dépasser, quelle que soit d'une part la machine employée à recevoir l'action de l'eau, et quelle que soit de l'autre la substance employée à recevoir l'action de la chaleur. La puissance motrice d'une chute d'eau dépend de sa hauteur et de la quantité du liquide; la puissance motrice de la chaleur dépend aussi de la quantité de calorique employé, et de ce ... que nous appellerons en effet la hauteur de sa chute, c'est-à-dire de la différence de température...

Fig. 3.5. Sadi Carnot. His reflections about the fall of heat¹⁴

This misconception, and the false information, which Carnot had about the specific heat of gases, and the latent heat of water vapour, invalidates much of the second half of his paper.¹⁵ He tied himself into knots over the specific heats of gases, which he thinks he can prove to be logarithmic functions of the density when in reality they are constants, independent of both density and temperature.

However, Carnot did ask the right questions. Thus he was interested to know how the location of the temperature *range* of the Carnot engine affected the efficiency. He states that *a given fall of the caloric* [a given temperature difference] *produces more motive power at inferior than at superior temperatures*.¹⁶ This is true, but unfortunately Carnot invalidates the statement in his marginal analysis,¹⁷ where he proves that – for temperature-independent specific heats – the efficiency is *independent* of the temperature range. The whole argument is a mess.

The best concrete result, which Carnot reached, concerned a Carnot engine working in the infinitesimal temperature range dt at t . In his notation the efficiency e is given by $e = F'(t)dt$, where $F'(t)$ is a universal function, sometimes called the *Carnot function*. Carnot could not determine that function. Thus, although he proved that the efficiency of a Carnot engine is maximal, he did not know the value of the maximum, – not even for an infinitesimal cycle. The Carnot function, however, partly because of its universal character, provided a strong stimulus for further research on the

¹⁴ S. Carnot: “Réflexions...” loc.cit. p. 28.

¹⁵ Carnot refers repeatedly to the experimental results of MM. Delaroche and Bérard, who thought that they had measured the specific heat of air to be dependent on pressure. We recall that Mayer was led to a wrong value of the mechanical equivalent of heat by measurements of the same two men, see Chap. 2.

¹⁶ S. Carnot: “Réflexions...” loc.cit. p. 72.

¹⁷ S. Carnot: *ibidem* pp. 73–78.

subject. Both Clapeyron and Kelvin recognized the need to know the values of that function, but were frustrated in their attempts to either measure or calculate it, cf. Inserts 3.1, 3.2. The problem was left open for Clausius to solve – twenty five years after Carnot.

It seems likely that Carnot, before publication of his work, did have second thoughts about the validity of his “Reflections”, particularly about the caloric theory. E. Mendoza who has had access to Carnot’s manuscript, quotes Carnot’s *original* summary, where Carnot concludes: *The fundamental law that we have proposed ... seems to us to have been placed beyond doubt.*¹⁸ In the *published* version this triumphant sentence is replaced by the more thoughtful one: *The fundamental law that we have proposed seems to us to require ... new verification. It is based upon the theory of heat as it is understood today ... [whose] foundation does not appear to be of unquestionable solidity.*

Carnot died in 1832 at the age of 36 years in a cholera epidemic. He left behind unpublished notes, in which he shows himself sceptical of the caloric theory,¹⁹ and where he speculates • on the conversion of heat into work, • on the conservation of *motion*, and • on the impossibility to produce work by cooling a heat bath without transmitting heat to a reservoir of lower temperature. Had he lived longer, it seems likely that he might have anticipated Clausius’s work by nearly 30 years.

As it was, however, his book which he tried to sell for 3 francs, found no readers and Carnot would have been entirely forgotten, perhaps, were it not for Clapeyron, like Carnot a former student of the École Polytechnique.

Benoît Pierre Émile Clapeyron (1799–1864)

Mendoza²⁰ writes that the list of men associated with the early period of the École Polytechnique in Paris – founded in 1794 as a school for army engineers – reads like the author index of a book on mathematical physics. *Among the first instructors were Lagrange, Fourier, Laplace, Berthollet, Ampère, Malus, and Dulong; among former students who stayed on as instructors were Cauchy, Arago, Désormes, Coriolis, Poisson, Gay-Lussac, Petit, and Lamé; other students included Fresnel, Biot, Sadi Carnot, and Clapeyron.* Maybe Clapeyron is not the most eminent one among these men, but his contribution was competent and he is remembered for it.

¹⁸ E. Mendoza: Footnote to Carnot’s “Reflections”: Dover (1960) loc.cit p. 46.

¹⁹ E. Mendoza (ed.): Appendix to Carnot’s “Reflections”: Selection from the posthumous manuscripts of Carnot: Dover (1960) loc.cit. p. 60.

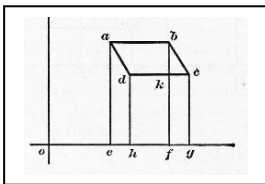
²⁰ E. Mendoza : Introduction to Carnot’s “Reflections” Dover loc.cit. p. ix.

Clapeyron's work²¹ is a big step forward from Carnot in clarity, but it marks time with respect to the caloric theory. An interesting feature of the work is the introduction of the graphical representation of reversible thermodynamic processes in a (pressure,volume)-diagram, such that the work of the process equals the area below its graph. This is a method of visualization which is still used today, see Fig. 3.4 above. Apart from that, Clapeyron's *analysis* is also perfect. I believe that his paper could have become a classic, if only the physics had not been below par.

However, even so, for some arguments involving heat, it does not matter whether heat is caloric or *motion*. Thus Clapeyron was able to establish a valid relationship between the slope of the vapour pressure curve $p(t)$ and the latent heat, or heat of evaporation $R(t)$, see Insert 3.1. That relation contains the Carnot function $F'(t)$ and it makes it possible to find the values of that function, if only $R(t)$ and $p(t)$ are measured. Extensive measurements of that type were published by Regnault²² in 1847, but that did not help Clapeyron in 1834, of course. His results remain indeterminate, because as he says *...unfortunately there are no experiments which allow us to determine the values of that function [the Carnot function] at all values of the temperature.*

The Clausius-Clapeyron equation

Clapeyron considered a Carnot process of wet steam. That process consists of horizontal isobars and steep adiabates. The isobars are also isotherms, since the vapour pressure depends only on temperature: $p = p(t)$. If the process is infinitesimal – with the temperature difference dt , and the evaporation of the mass fraction dx of liquid water on the isothermal branch – we have



$R \, dx$ – for the heat absorbed, and
 $\frac{dp}{dt} dt [(V'' - V')dx]$ – for the work done.

Fig. 3.6. (p, V) -diagram of infinitesimal Carnot process in wet steam

R is the latent heat of evaporation and dp is the height of the small cycle, cf. Fig. 3.6.

²¹ E. Clapeyron: “Mémoire sur la puissance motrice de la chaleur” Journal de l’École Polytechnique. Vol XIV (1834) pp. 153–190. Translations: (English) “Memoir on the motive power of heat.” Scientific Memoirs Vol. 1 (1837) pp. 347–376. (German) “Über die bewegende Kraft der Wärme.” Annalen der Physik und Chemie Vol 135 (1843).

²² H.V. Regnault: “Relations des expériences ...pour déterminer les principales lois et les données numériques qui entrent dans le calcul des machines à vapeur.” Mémoires de l’Académie des Sciences de l’Institut de France, Paris, Vol. 21 (1847) pp. 1–748.

V' and V'' are the volumes of the boiling water and of the saturated vapour of which the wet steam is composed.

The ratio of the two quantities is the efficiency e . And by Carnot's results it is equal to $e = F'(t)dt$, see above. Therefore we have

$$\frac{dp}{dt} = F'(t) \frac{R}{V'' - V'}.$$

Thus Carnot's universal function could be calculated from measurements of R , of $\frac{dp}{dt}$, – the slope of the vapour pressure curve – and of the vapour volume V'' , all at temperature t . Kelvin attempted such calculations, see below.

Clausius found later – in 1850, cf. Insert 3.3 – that $F'(t)$ equals $\frac{1}{T}$, where T is the absolute temperature, and therefore the relation

$$\frac{dp}{dT} = \frac{R}{T(V'' - V')}$$

is called the Clausius-Clapeyron relation. Nowadays it is used to calculate the latent heat R of a new refrigerant (say) from the vapour pressure curve; the latter is easier to measure than R .

Insert 3.1

William Thomson (1824–1907), Lord Kelvin since 1892

Kelvin has accompanied the development of thermodynamics for more than half a century, starting from his graduation in 1845. He went to Paris after graduation to work and study under Regnault, the careful and influential experimenter, whom we have already mentioned. Later Kelvin encouraged and supported Joule, and together the two men discovered the Joule-Thomson effect in real gases, see Chaps. 2 and 6. Kelvin suggested the absolute temperature scale that bears his name, and he was a forerunner of the second law with the idea that there is a continuous degradation, or dissipation of energy into heat. However, Kelvin missed out himself on the *paradigmatic changes*²³ in thermodynamics. To be sure, when they occurred, he was often the first, or one of the first, to interpret and rephrase them, and apply them. Therefore a history of thermodynamics is incomplete without a prominent place for Kelvin. Perhaps his greatest achievement is that he suggested the possibility of *convective equilibrium*, see Chap. 7,

²³ This term has been made popular by Thomas S. Kuhn in his book: “The structure of scientific revolutions.” The University of Chicago Press, Chicago and London. Third edition (1996).

which goes a long way to determine the structure of stars and the conditions in the lower atmosphere of the earth. Another original result of his is the Thomson formula for super-saturation in the processes of boiling and condensation on account of surface energy. However, here I choose to highlight Kelvin's capacity for original thought by a proposition he made for an absolute temperature scale, – an alternative to the Kelvin scale which we all know; see Insert 3.2. The proposition is intimately linked to the Carnot function $F'(t)$ which Kelvin attempted to calculate from Regnault's data. The new scale would have been logarithmic, and *absolute zero* would have been pushed to $-\infty$, a fact that gives the proposition its charm.

Kelvin's alternative absolute temperature scale

We recall the Carnot function $F'(t)$, a universal function of the temperature t , which neither Carnot nor Clapeyron had been able to determine. After Regnault's data were published, Kelvin used them to calculate $F'(t)$ for 230 values of t between 0°C and 230°C .²⁴ He proposed to rescale the temperature, and to introduce $\tau(t)$ such that the Carnot efficiency $F'(t)dt$ for a small *fall* dt of *caloric* would be equal to $cd\tau$, where c is a constant, independent of t or τ . Kelvin found that feature appealing. He says: *This [scale] may justly be termed an absolute scale*. By integration $\tau(t)$ results as

$$\tau(t) = \tau(0) + \frac{1}{c} \int_0^t F'(x) dx \cdot$$

Had Kelvin been able to fit an analytic function to Regnault's data, and to his calculations of $F'(t)$, he would have found a hyperbola

$$F'(t) = \frac{1}{273^\circ\text{C} + t}$$

and his new scale would have been logarithmic:

$$\tau(t) = \tau(0) + \frac{1}{c} \ln \frac{273^\circ\text{C} + t}{273^\circ\text{C}} \cdot$$

$\tau(0)$ and c need to be determined by assigning τ -values to two fix-points, e.g. melting ice and boiling water.

However, not even the 230 values, which Kelvin possessed, were good enough to suggest the hyperbola in a convincing manner.

Therefore Kelvin had to wait for Clausius to determine $F'(t)$ in 1850, cf. Insert 3.3. When Kelvin's papers were reprinted in 1882, he added a note in which indeed he proposes the logarithmic temperature scale.

²⁴ W. Thomson: "On the absolute thermometric scale founded on Carnot's theory of the motive power of heat, and calculated from Regnault's observations." *Philosophical Magazine*, Vol. 33 (1848) pp. 313–317.

Compared to this daring proposition Kelvin's previous introduction of the absolute scale $T(t) = (273 + \frac{t}{^{\circ}\text{C}})^{\circ}\text{K}$ seems straightforward, and rather plain. As it was, however, the logarithmic scale was never seriously considered, not even by Kelvin.

One might think that nobody really wanted the temperature scale on a thermometer to look like a slide rule. Yet, in the meteorological range between -30°C and $+50^{\circ}\text{C}$ the function $\tau(t)$ is nearly linear. And also, for $t \rightarrow -273^{\circ}\text{C}$ the rescaled temperature τ tends to $-\infty$, which is not a bad value for the absolute minimum of temperature. One could almost wish that Kelvin's proposition had been accepted. That would make it easier to explain to students why the minimum temperature cannot be reached.

Insert 3.2

Rudolf Julius Emmanuel Clausius (1822–1888)

By 1850 the efforts of Rumford, Mayer, Joule and Helmholtz had finally succeeded to create an overwhelming feeling that something was wrong with the idea that heat passes from boiler to cooler *unchanged in amount*: Some of the heat, in the passage, ought to be converted to work. But how to implement that new knowledge? Kelvin despaired:²⁵ *If we abandon [Carnot's] principle we meet with innumerable other difficulties ... and an entire reconstruction of the theory of heat [is needed].*

Clausius was less pessimistic:²⁶ *I believe we should not be daunted by these difficulties. ... [and] then, too, I do not think the difficulties are so serious as Thomson [Kelvin] does.* And indeed, it took Clausius surprisingly slight touches in surprisingly few spots of Carnot's and Clapeyron's works to come up with an expression for the Carnot function $F'(t)$ which determines the efficiency e of a Carnot cycle between t and $t+dt$. We recall that Carnot had proved $e=F'(t)dt$. And Clausius was the first person to argue convincingly that $F'(t) = \frac{1}{273^{\circ}\text{C}+t} = \frac{1}{T}$ holds, cf.

Insert 3.3.

²⁵ W. Thomson: "An account of Carnot's theory of the motive power of heat." Transactions of the Royal Society of Edinburgh 16 (1849). pp. 5412–574.

²⁶ R. Clausius: "Über die bewegende Kraft der Wärme und die Gesetze, welche sich daraus für die Wärme selbst ableiten lassen." Annalen der Physik und Chemie 155 (1850). pp. 368–397. Translation by W.F. Magie: "On the motive power of heat, and on the laws which can be deduced from it for the theory of heat." Dover (1960). Loc.cit. pp. 109–152.

Clausius's derivation of the internal energy and the calculation of the Carnot function

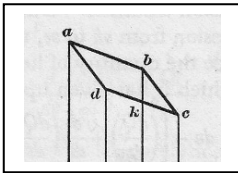
When a body absorbs the heat dQ it changes the temperature by dt and the volume by dV , as dictated by the heat capacity C_v and the latent heat λ ²⁷ so that we have

$$dQ = C_v(t, V) dt + \lambda(t, V) dV.$$

Truesdell, who had the knack of a pregnant expression, calls this equation the *doctrine of the latent and specific heat*.²⁸ Applied to an infinitesimal Carnot process $abcd$ this reads, cf. Fig. 3.7:

$$\begin{array}{ll} ab \cong (dV, dt=0) & dQ_{ab} = \boxed{C_v(t, V)} dt + \lambda(t, V) dV \\ bc \cong (\delta'V, dt) & \boxed{dQ_{bc}} = -C_v(t, V+dV) dt + \lambda(t, V+dV) \delta'V \\ cd \cong (d'V, dt=0) & dQ_{cd} = \boxed{C_v(t-dt, V+\delta V) d'V} - \lambda(t-dt, V+\delta V) d'V \\ da \cong (\delta V, dt) & \boxed{dQ_{da}} = C_v(t, V) dt - \lambda(t, V) \delta V \end{array}$$

All framed quantities are zero, since the process is composed of isotherms and adiabates. Thus with a little calculation – expanding the coefficients – Clausius arrived at formulae for



$$\text{heat exchanged: } dQ_{ab} + dQ_{cd} = \left(\frac{\partial \lambda}{\partial t} - \frac{\partial C_v}{\partial V} \right) dt dV$$

$$\text{heat absorbed: } dQ_{ab} = \lambda dV$$

$$\text{work done: } dp dV = \frac{\partial p}{\partial t} dV dt.$$

Fig. 3.7. (p, V) -diagram of an infinitesimally small Carnot cycle in a gas.

The work was calculated as the area of the parallelogram.

By the first law the heat exchanged equals the work done: Hence

$$\frac{\partial \lambda}{\partial t} - \frac{\partial C_v}{\partial V} = \frac{\partial p}{\partial t} \quad \text{or} \quad \frac{\partial(\lambda - p)}{\partial t} - \frac{\partial C_v}{\partial V} = 0$$

which may be considered as the integrability condition of the differential form

$$dU = C_v dt + (\lambda - p) dV \quad \text{or} \quad dU = dQ - p dV.$$

Thus Clausius arrived at the notion of the state function *internal energy* U , generally a function of t and V . Clausius assumed – correctly – that *in an ideal gas* U depends only on t . Therefore $\lambda = p$ holds and the efficiency e of the Carnot process is

²⁷ In modern thermodynamics the term *latent heat* is reserved as a generic expression for the heat of a phase transition – like heat of melting, or heat of evaporation –, but this was not so in the 19th century.

²⁸ C. Truesdell: “The tragicomical History of Thermodynamics 1822–1854”. Springer Verlag New York (1980) [The specific heat is the heat capacity per mass.].

$$e = \frac{\text{work done}}{\text{heat absorbed}} = \frac{\frac{m}{V} \frac{k}{\mu}}{\lambda} dt = \frac{1}{273^\circ\text{C} + t} dt$$

and the universal Carnot function $F'(t)$ is now calculated once and for all:

$$F'(t) = \frac{1}{273^\circ\text{C} + t} = \frac{1}{T}.$$

[It is true that Clausius in 1850 calculated the *work done* only for an ideal gas. The above generalization to an arbitrary fluid came in 1854.²⁹]

Insert 3.3

Notation and mode of reasoning of Clausius is nearly identical to that of Clapeyron with the one difference, – an essential difference indeed – that the total heat exchange of an infinitesimal Carnot cycle is not zero; rather it is equal to the work. Thus the heat Q is not a *state function* anymore, i.e. a function of t and V (say). To be sure, there *is* a state function, but it is not Q . Clausius denotes it by U , cf. Insert 3.3, and he calls U the *sum of the free heat and of the heat consumed in doing internal work*, meaning the sum of the kinetic energies of all molecules and of the potential energy of the intermolecular forces.³⁰ Nowadays we say that U is the *internal energy* in order to distinguish it from the kinetic energy of the flow of a fluid and from the potential energy of the fluid in a gravitational field.

A change of U is either due to heat exchanged or work done, or both:

$$dU = dQ - pdV.$$

With this relation the first law of thermodynamics finally left the compass of verbiage – like *heat is motion* or *heat is equivalent to work*, or *impossibility of the perpetuum mobile*, etc. – and was cast into a

²⁹ R. Clausius: “Über eine veränderte Form des zweiten Hauptsatzes der mechanischen Wärmetheorie”. *Annalen der Physik und Chemie* 169 (1854). English translation: “On a modified form of the second fundamental theorem in the mechanical theory of heat.” *Philosophical Magazine* (4) 12, (1856).

³⁰ It was Kelvin who, in 1851, has proposed the name energy for U : W. Thomson: “On the dynamical theory of heat, with numerical results deduced from Mr. Joule’s equivalent of a thermal unit, and M. Regnault’s observations on steam.” *Transactions of the Royal Society of Edinburgh* 20 (1851). p. 475.

Clausius concurred: ... *in the sequel I shall call U the energy*. It is quite surprising that Clausius let himself be preceded by Kelvin in this matter, because Clausius himself was an inveterate name-fixer. He invented the *virial* for something or other in his theory of real gases, see Chap. 6, and he proposed the *ergal* as a word for the potential energy, which seemed too long for his taste. And, of course, he invented the word *entropy*, see below.

mathematical equation, albeit for the special case of reversible processes and for a closed system, i.e. a body of fixed mass.

Clausius reasonably – and correctly – assumes that U is independent of V in an ideal gas and a linear function of t , so that the specific heats are constant. Because, he says: *...we are naturally led to take the view that the mutual attraction of the particles... no longer acts in gases*, so that U does not *feel* how far apart the particles are, or how big the volume is. For an ideal gas we may write³¹

$$U(T,V) = U(T_R) + m z \frac{k}{\mu} (T - T_R),$$

where T_R is a reference temperature, usually chosen as 298K. The factor z has the value $\frac{3}{2}$, $\frac{5}{2}$, and 3 for one-, two-, or more-atomic gases respectively.

Actually Clausius could have proved his *view* – at least as far as it relates to the V -independence of U – from Gay-Lussac's experiment, mentioned in Chap. 2, on the adiabatic expansion of an ideal gas into an empty volume, where U must be unchanged after the process, and the temperature is *observed* to be unchanged, although the density does change, of course. As it is, Clausius mentions the (p,V,t) -relation of Mariotte and Gay-Lussac on every second page, but he seems to be unaware of Gay-Lussac's expansion experiment, or he does not recognize its significance.

In his paper of 1850, which we are discussing, Clausius deals with ideal gases and saturated vapour. Having determined the universal Carnot function, he is able to write the Clausius-Clapeyron equation, cf. Insert 3.1. Also he can obtain the adiabatic (p,V,t) -relation in an ideal gas, whose prototype is $pV^\gamma = \text{const}$, – well-known to all students of thermodynamics – where $\gamma = C_p/C_v$ is the ratio of specific heats. Later, in 1854,³² Clausius applies this knowledge to calculate the efficiency e of a Carnot cycle of an ideal gas in any range of temperature, no matter how big; certainly not infinitesimal. He obtains, cf. Insert 3.4

$$e = 1 - \frac{T_{Low}}{T_{High}},$$

so that even the maximal efficiency is smaller than one, unless $T_{Low} = 0$ holds of course, which, however, is clearly impractical.

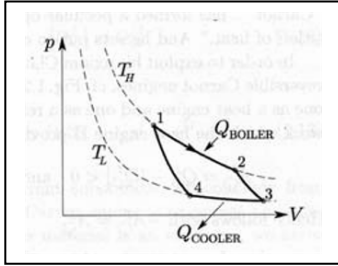
³¹ This is a modern version which, once again, is somewhat anachronistic. Clausius was concerned with air and he used the poor value of the specific heat – given by Delaroche and Bérard – which had already haunted the works of Carnot and Mayer.

To do full justice to the specific heats, even of ideal gases, one could write a book all by itself. But that would be a different book from the present one.

³² R. Clausius: (1854) loc.cit.

Efficiency of a Carnot cycle of a monatomic ideal gas

We refer to Fig. 3.8 which shows a graphical representation of a Carnot cycle between temperatures T_{High} and T_{Low} . For a monatomic ideal gas we have for the work and the heat exchanged on the four branches



$$W_{12} = -m \frac{k}{\mu} T_H \ln \frac{V_2}{V_1}, \quad Q_{12} = m \frac{k}{\mu} T_H \ln \frac{V_2}{V_1}$$

$$W_{23} = m \frac{3k}{2\mu} (T_L - T_H), \quad Q_{23} = 0$$

$$W_{34} = -m \frac{k}{\mu} T_L \ln \frac{V_4}{V_3}, \quad Q_{34} = -m \frac{k}{\mu} T_L \ln \frac{V_4}{V_3}$$

Fig. 3.8 Graph of a Carnot process $W_{41} = m \frac{3k}{2\mu} (T_H - T_L), \quad Q_{41} = 0$

Therefore the efficiency comes out as

$$e = \frac{m \frac{k}{\mu} T_H \ln \frac{V_2}{V_1} + m \frac{k}{\mu} T_L \ln \frac{V_4}{V_3}}{m \frac{k}{\mu} T_H \ln \frac{V_2}{V_1}} = 1 - \frac{T_L}{T_H}.$$

The last equation results from the observation that $\frac{V_2}{V_1} = \frac{V_3}{V_4}$ holds.

Insert 3.4

With all this – by Clausius’s work of 1850 – thermodynamics acquired a distinctly modern appearance. His assumptions were quickly confirmed by experimenters,³³ or by reference to older experiments, which Clausius had either not known, or not used. Nowadays a large part of a modern course on thermodynamics is based on that paper by Clausius: the part that deals with ideal gases, and a large portion of the part on wet steam.

For Clausius, however, that was only the beginning. He proceeded with two more papers^{34,35} in which he took five important steps forward:

³³ W. Thomson, J.P. Joule: “On the thermal effects of fluids in motion.” Philosophical Transactions of the Royal Society of London 143 (1853).

³⁴ R. Clausius: (1854) loc.cit.

³⁵ R. Clausius: “Über verschiedene für die Anwendungen bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie”. Poggendorff’s Annalen der Physik 125 (1865). English translation by R.B. Lindsay: “On different forms of the fundamental equations of the mechanical theory of heat and their convenience for application”. In: “The Second Law of Thermodynamics.” J. Kestin (ed.), Stroudsburg (Pa), Dowden Hutchinson and Ross (1976).

• away from infinitesimal Carnot cycles • away from ideal gases • away from Carnot cycles altogether, • away from cycles of whatever type, and • away from reversible processes.³⁶ In the end he came up with the concept of entropy and the properties of entropy, and that is his greatest achievement. We shall presently review his progress.

Among the people, whom we are discussing in this book, Clausius was the first one who lived and worked entirely in the place that was to become the natural habitat of the scientist: The autonomous university with tenured professors,³⁷ often as public or civil servants. With Clausius the time of *doctor-brewer-soldier-spy* had come to an end, at least in thermodynamics. General and compulsory education had begun and universities sprang up to satisfy the need for higher education and they had to be staffed. Thus one killed two birds with one stone: When a professor was no good as a scientist, he could at least teach and thus earn part of his keep. On the other hand, if he was good, the teaching duties left him enough time to do research.³⁸ Clausius belonged to the latter category. He was a professor in Zürich and Bonn, and his achievements are considerable: He helped to create the kinetic theory of ideal and real gases and, of course, he was the discoverer of entropy and the second law. His work on the kinetic theory was largely eclipsed by the progress made in that field by Maxwell in England and Boltzmann in Vienna. And in his work on thermodynamics he had to fight off numerous objections and claims of priority by other people, who had thought, or said, or written something similar at about the same time. By and large Clausius was successful in those disputes. Brush calls Clausius *one of the outstanding physicists of the nineteenth century*.³⁹

³⁶ Reversible processes are those – in the present context of single fluids – in which temperature and pressure are always homogeneous, i.e. spatially constant, throughout the process, and therefore equal to temperature and pressure at the boundary. If that process runs backwards in time, the heat absorbed is reversed (sic) into heat emitted, or vice versa. A hallmark of the reversible process is the expression $-pdV$ for the work dW . That expression for dW is not valid for an irreversible process, which may exhibit turbulence, shear stresses and temperature gradients inside the cylinder of an engine (say) during expansion or compression. Irreversibility usually results from rapid heating and working.

³⁷ Tenure was intended to protect freedom of thought as much as to guarantee financial security.

³⁸ The system worked fairly well for one hundred years before it was undermined by job-seekers or frustrated managers, who failed in their industrial career. They are without scientific ability or interest, and spend their time attending committee meetings, reformulating curricula, and tending their gardens.

³⁹ Stephen G. Brush: “Kinetic Theory” Vol I. Pergamon Press, Oxford (1965).

Second Law of Thermodynamics

Clausius keeps his criticism of Carnot mild when he says that ... *Carnot has formed a peculiar opinion* [of the transformation of heat in a cycle]. He sets out to correct that opinion, starting from an axiom which has become known as the *second law of thermodynamics*:

Heat cannot pass by itself from a colder to a warmer body.

This statement, suggestive though it is, has often been criticized as vague. And indeed, Clausius himself did not feel entirely satisfied with it. Or else he would not have tried to make the sentence more rigorous in a page-long comment, which, however, only succeeds in removing whatever suggestiveness the original statement may have had.⁴⁰ We need not go deeper into this because, after all, in the end there will be an unequivocal *mathematical* statement of the second law.

The technique of exploitation of the axiom makes use of Carnot's idea of letting two reversible Carnot machines compete, – one a heat engine and the other one a heat pump, or refrigerator, cf. Fig. 3.9; the pump becomes an engine when it is reversed and *vice versa*; and the heats exchanged are changing sign upon reversal. Both machines work in the temperature range between T_{Low} and T_{High} and one produces the work which the other one consumes, cf. Fig. 3.9. Thus Clausius concludes that both machines must exchange the same amounts of heat at both temperatures, lest heat flow from cold to hot, which is forbidden by the axiom. So the efficiencies of both machines are equal, – if they work as heat engines. And, since nothing is said about the working agents in them, the efficiency must be universal. So far this is all much like Carnot's argument.

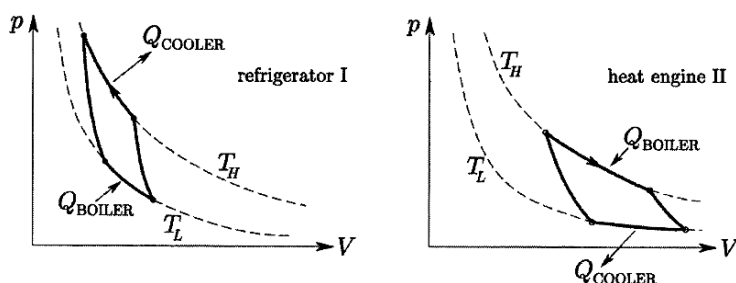


Fig. 3.9. Clausius's competing reversible Carnot engines

⁴⁰ E.g. see R. Clausius: "Die mechanische Wärmetheorie" [The mechanical theory of heat] (3.ed.) Vieweg Verlag, Braunschweig (1887) p. 34.

But then, unlike Carnot, Clausius knew that the work W_o of the heat engine is the difference between Q_{boiler} and $|Q_{cooler}|$ so that the efficiency of any engine, – not necessarily a reversible Carnot engine – is given by

$$e = \frac{W_o}{Q_{boiler}} = 1 - \frac{|Q_{cooler}|}{Q_{boiler}}.$$

Q_{cooler} could conceivably be zero; at least, if it were, that would not contradict the first law, which only forbids W_o to be *bigger* than Q_{boiler} . However, if the engine is a reversible Carnot engine with its universal efficiency, that efficiency is equal to that of an ideal gas – see above – so that we must have

$$\frac{Q_{boiler}}{T_{High}} = \frac{|Q_{cooler}|}{T_{Low}}.$$

It is clear from this equation that it is not the *heat* that passes through a Carnot engine unchanged in amount; rather it is Q/T , the *entropy*.

Clausius sees two types of *transformations* going on in the heat engine: The conversion of heat into work, and the passage of heat of high temperature to that of low temperature. Therefore in 1865⁴¹ he proposes to call $\frac{Q}{T}$ the *entropy*, ... after the Greek word *τροπή* = *transformation*, or *change* and he denotes it by S . He says that he has intentionally chosen the word to be similar to *energy*, because he feels that the two quantities ... *are closely related in their physical meaning*. Well, maybe they appeared so to Clausius. However, it seems very much the question, in what way two quantities with different dimensions can be *close*.

The last equation shows that $|Q_{cooler}|$ cannot be zero, except for the impractical case $T_{Low} = 0$. Thus even for the optimal engine – the Carnot engine – there must be a cooler. Far from getting *more* work than the heat supplied to the boiler, we now see that we cannot even get that much: The boiler heat cannot all be converted into work. Therefore we cannot gain work by just cooling a single heat reservoir, like the sea. Students of thermodynamics like to express the situation by saying, rather flippantly:

1st law: You cannot win.

2nd law: You cannot even break even.

All of this still refers to cycles, or actually Carnot cycles. In Insert 3.5 we show in the shortest possible manner, how Clausius extrapolated these results to arbitrary cycles, and how he was able to consolidate the notion of entropy as a state function $S(T,V)$, whose significance is not restricted to cycles. The final result is the mathematical expression of the second law

⁴¹ R. Clausius: (1865) loc.cit.

and it is an *inequality*: For a process from (T_B, V_B) to (T_E, V_E) the entropy growth cannot be smaller than the sum of heats exchanged divided by the temperature, where they are exchanged:

$$S(T_E, V_E) - S(T_B, V_B) \geq \int_B^E \frac{dQ}{T} \quad [\text{equality holds for reversible processes}].$$

Clausius's derivation of the second law

Since $Q_{\text{cooler}} < 0$, the relation

$$\frac{Q_{\text{boiler}}}{T_{\text{High}}} = \frac{|Q_{\text{cooler}}|}{T_{\text{Low}}} \quad \text{may be written as} \quad \frac{Q_{\text{boiler}}}{T_{\text{High}}} + \frac{Q_{\text{cooler}}}{T_{\text{Low}}} = 0 \quad .$$

In order to extrapolate this relation away from Carnot cycles to arbitrary cycles, Clausius decomposed such an arbitrary cycle into Carnot cycles with infinitesimal isothermal steps, cf. Fig.3.10. On those steps the heat dQ is exchanged such that $dS = dQ/T$ is passing from the warm side to the cold one. Summation – or integration – thus leads to the equation

$$\oint dS = \oint \frac{dQ}{T} = 0$$

Hence follows for an open reversible process – not a cycle – between the points B and E

$$S(T_E, V_E) - S(T_B, V_B) = \int_B^E \frac{dQ}{T} ,$$

where $S(T_E, V_E) - S(T_B, V_B)$ is independent of the path from B to E , so that the entropy function $S(T, V)$ is a *state function*. After the internal energy $U(T, V)$ this is the second state function discovered by Clausius.

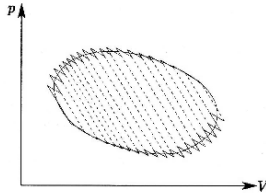


Fig. 3.10. Smooth cycle decomposed into narrow Carnot cycles

It remains to learn how this relation is affected by irreversibility. For that purpose Clausius reverted to the two competing Carnot engines, – one driving the other one. But now, one of them, the heat engine, was supposed to work irreversibly. In that case the process in the heat engine cannot be represented by a

graph in a (p,V) -diagram, and therefore we show it *schematically* in Fig. 3.11. It turns out that the system of two engines contradicts Clausius's axiom, if the heat pump absorbs more heat at the low temperature than the heat engine delivers there. And now the reverse case cannot be excluded, because the engine changes its heat exchanges when it is made to work as a pump. Therefore for the irreversible heat engine we have

$$\frac{Q_{boiler}}{T_{High}} + \frac{Q_{cooler}}{T_{Low}} < 0,$$

It follows that the efficiency of the irreversible engine is lower than that of the reversible engine, and *a fortiori* – by the same sequence of arguments as before – that in an arbitrary irreversible process between points B and E we have

$$S(T_E, V_E) - S(T_B, V_B) > \int_B^E \frac{dQ}{T}.$$

The two relations for the change of entropy – one for the reversible and the other for the irreversible process – may be combined in a single \geq alternative, as we have done in the main text..

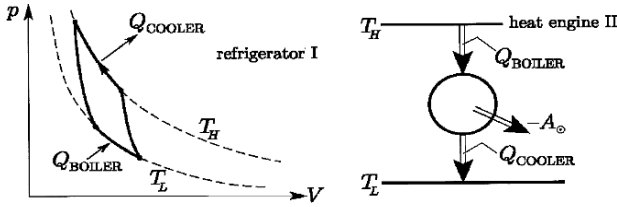


Fig. 3.11. Two competing Carnot engines with an irreversible heat engine

Insert 3.5

Exploitation of the Second Law

An important corollary of the second law concerns a reversible process between B and E , when those two point are infinitesimally close. In that case we have

$$dS = \frac{dQ}{T}$$

and when we eliminate dQ between that relation and the first law in the form $dQ = (dU + pdV)$, we obtain

$$dS = \frac{1}{T} (dU + pdV).$$

This equation is called the *Gibbs equation*.⁴² Its importance can hardly be overestimated; it saves time and money and it is literally worth billions to the chemical industry, because it reduces drastically the number of measurements, which must be made in order to determine the internal energy $U = U(T, V)$ as a function of T and V .

Let us consider this:

Both the *thermal equation of state* $p = p(T, V)$ and the *caloric equation of state* $U = U(T, V)$ are needed explicitly for the calculation of nearly all thermodynamic processes, and they must be measured. Now, it is easy – at least in principle – to determine the thermal equation, because p , T , and V are all measurable quantities and they need only be put down in tables, or diagrams, or – in modern times – on CD's. But that is not so with the caloric equation, because U is not measurable. $U(T, V)$ must be calculated from caloric measurements of the heat capacities $C_v(T, V)$ and $C_p(T, V)$. Such measurements are difficult and time-consuming, – hence expensive – and they are unreliable to boot. And this is where the Gibbs equation helps. It helps to reduce – drastically – the number of caloric measurements needed, cf. Insert 3.6 and Insert 3.7.

Calculating $U(T, V)$ from measurements of heat capacities

The heat capacities C_v and C_p are defined by the equation $dQ = CdT$. Thus they determine the temperature change of a mass for a given application of heat dQ at either constant V or p . In this way C_v and C_p can be measured. By $dQ = dU + p dV$, and since we do know that U is a function of T and V – we just do not know the form of that function – we may write

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v \quad \text{and} \quad C_p = \left(\frac{\partial U}{\partial T} \right)_p + \left(\left(\frac{\partial U}{\partial V} \right)_T + p \right) \left(\frac{\partial V}{\partial T} \right)_p \quad \text{or}$$

$$\left(\frac{\partial U}{\partial T} \right)_v = C_v \quad \text{and} \quad \left(\frac{\partial U}{\partial V} \right)_T = \frac{C_p - C_v}{\left(\frac{\partial V}{\partial T} \right)_p} - p.$$

Having measured $C_v(T, V)$ and $C_p(T, V)$ and $p(T, V)$ we may thus calculate $U(T, V)$ by integration to within an additive constant.

The integrability condition implied by the Gibbs equation provides

$$\frac{\partial U}{\partial V} = -p + T \frac{\partial p}{\partial T}.$$

Hence follows that the V -dependence of U , hence C_p , need not be measured: It may be calculated from the thermal equation of state. Moreover, differentiation with respect to T provides the equation

⁴² Actually the equation was first written and exploited by Clausius, but Gibbs extended it to mixtures, see Chap. 5; the extension became known as *Gibbs's fundamental equation* and, as time went by, that name was also used for the special case of a single body.

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V,$$

so that the V -dependence of C_V is also determined by $p(T, V)$. Therefore the only caloric measurements needed are those of C_V as a function of T for *one* volume, V_0 (say). The number of caloric measurements is therefore considerably reduced, and that is a direct result of the Gibbs equation and the second law.

Insert 3.6

Once we know the thermal and caloric equations of state we may calculate the entropy $S(T, V)$, or $S(T, p)$ – by integration of the Gibbs equation – to within an additive constant. Thus for an ideal gas of mass m we obtain

$$S(T, p) = S(T_r, p_r) + m \left((z+1) \frac{k}{\mu} \ln \frac{T}{T_r} - \frac{k}{\mu} \ln \frac{p}{p_r} \right).$$

Therefore the entropy of an ideal gas grows with $\ln T$ and $\ln V$: The isothermal expansion of a gas increases its entropy.

Clausius-Clapeyron equation revisited

If the Gibbs equation is applied to the reversible evaporation of a liquid under constant pressure – and temperature – it may be written in the form

$$(U-TS+pV)'' = (U-TS+pV)',$$

where, once again, ' and '' characterize liquid and vapour. Thus the combination $U-TS+pV$, called *free enthalpy* or *Gibbs free energy*, is continuous across the interface between liquid and vapour, along with T and p . Therefore the vapour pressure must be a function of temperature only. We have $p=p(T)$ and the derivative of that function is given by the Clausius-Clapeyron equation, cf. Insert 3.1. When we realize that the heat of evaporation equals $R=T(S''-S')$, we may write the Clausius-Clapeyron equation in the form

$$\frac{U''-U'}{V''-V'} = -p + T \frac{dp}{dT},$$

which is clearly – for steam – the analogue to the integrability condition of Insert 3.6. The relation permits us to dispense with measurements of the latent heat of steam and to replace them with the much easier (p, T) -measurements.

Insert 3.7

There is a school of thermodynamicists – the axiomatists – who thrive on formal arguments, and who would never let considerations of measurability enter their thoughts.⁴³ One can hear members of that school say, that the temperature T is

⁴³ Such an attitude is not uncommon in other branches of physics as well. Thus in mechanics there is a school of thought that considers Newton's law $F = m a$ as the definition of the force rather than a physical law between measurable quantities.

defined as $(\frac{\partial U}{\partial S})_V$. That interpretation of the Gibbs equation ignores the fact that we should never know anything about either U or S , let alone $U=U(S,V)$, unless we had determined them first by measurements of p, V, T , and $C_V(T, V_0)$ in the manner described above.

Actually, the measurability of T is a consequence of its continuity at a diathermic wall, i.e. a wall permeable for heat. That continuity is the *real* defining property of temperature, and it gives temperature its central role in thermodynamics.

The chief witness of the formal interpretation of temperature is Gibbs, unfortunately, the illustrious pioneer of thermodynamics of mixtures. He, however, for all his acumen, was an inveterate theoretician, and I believe that he never made a single thermodynamic measurement in his whole life. We shall come back to this discussion in the context of chemical potentials, cf. Chap. 5, which have a lot in common with temperature.

Continuing our discussion of the consequences of the second law, we now come to another important corollary, namely that the *entropy in an adiabatic process*, – where $dQ = 0$ holds –, *cannot decrease*. It grows until it reaches a maximum. We know from experience that, when we leave an adiabatic system alone, it tends to a state of homogeneity – the *equilibrium*, – in which all driving forces for heat conduction and expansion have run down.⁴⁴ That is the state of maximum entropy.

And so Clausius could summarize his work in the triumphant slogan:⁴⁵

**Die Energie der Welt ist constant.
Die Entropie der Welt strebt einem Maximum zu.**

Die Welt [the universe] was chosen in this statement as being the ultimate thermodynamic system, which presumably is not subject to heating and working, so that $dU = 0$ holds, as well as $dS > 0$.

So the world has a purpose, or a destination, the *heat death*, see Fig. 3.12, not an attractive end!



It is often said that the world goes in a circle ... such that the same states are always reproduced. Therefore the world could exist forever. The second law contradicts this idea most resolutely ... The entropy tends to a maximum. The more closely that maximum is approached, the less cause for change exists. And when the maximum is reached, no further changes can occur; the world is then in a dead stagnant state.

Fig. 3.12. Rudolf Clausius and his contemplation of the heat death

⁴⁴ See Chap. 5 for a formal proof and for an explanation of what exactly homogeneity means.

⁴⁵ R. Clausius: (1865) loc.cit. p. 400.

Terroristic Nimbus of Entropy and Second Law

Concerning the heat death modern science does not seem to have made up its mind entirely. Asimov⁴⁶ writes:

Though the laws of thermodynamics stand as firmly as ever, cosmologists ...[show] a certain willingness to suspend judgement on the matter of heat death.

At his time, however, Clausius's predictions were much discussed. The teleological character of the entropy aroused quite some interest, not only among physicists, but also among philosophers, historians, sociologists and economists. The gamut of reactions ranged from uneasiness about the bleak prospect to pessimism confirmed. Let us hear about three of the more colourful opinions:

The physicist Josef Loschmidt (1821–1895)⁴⁷ deplored

... the terroristic nimbus of the second law ..., which lets it appear as a destructive principle of all life in the universe.⁴⁸

Oswald Spengler (1880–1936), the historian and philosopher of history devotes a paragraph of his book “The Decline of the West”⁴⁹ to entropy. He thinks that ... *the entropy firmly belongs to the multifarious symbols of decline*, and in the growth of entropy toward the heat death he sees the scientific equivalent of the *twilight of the gods* of Germanic mythology:

The end of the world as the completion of an inevitable evolution – that is the twilight of the gods. Thus the doctrine of entropy is the last, irreligious version of the myth.

And the historian Henry Adams (1838–1918) – an apostle of human degeneracy, and the author of a meta-thermodynamics of history – commented on entropy for the benefit of the *ordinary, non-educated historian*. He says:

.... this merely means that the ash-heap becomes ever bigger.

⁴⁶ I. Asimov: “Biographies” loc.cit. p. 364.

⁴⁷ J. Loschmidt: “Über den Zustand des Wärmegleichgewichts eines Systems von Körpern mit Rücksicht auf die Schwerkraft.” [On the state of the equilibrium of heat of a system of bodies in regard to gravitation.] Sitzungsberichte der Akademie der Wissenschaften in Wien, Abteilung 2, 73: pp. 128–142, 366–372 (1876), 75: pp. 287–298, (1877), 76: pp. 205–209, (1878).

⁴⁸ If the author of this book had had his way in the discussion with the publisher, this citation of Loschmidt would have been either the title or the subtitle of the book. But, alas, we all have to yield to the idiosyncrasies of our real-time terrorists, – and to the show of paranoia by our opinionators.

⁴⁹ O. Spengler: “Der Untergang des Abendlandes: Kapitel VI. Faustische und Apollinische Naturerkenntnis. § 14: Die Entropie und der Mythos der Götterdämmerung.” Beck'sche Verlagsbuchhandlung, München (1919) pp. 601–607.

Well, maybe it does. But then, Adams was an inveterate pessimist, to the extent even that he looked upon optimism as a sure symptom of idiocy.⁵⁰

The entropy and its properties have not ceased to stimulate original thought throughout science to this day:

- biologists calculate the entropy increase in the diversification of species,
- economists use entropy for estimating the distribution of goods,⁵¹
- ecologists talk about the dissipation of resources in terms of entropy,
- sociologists ascribe an entropy of mixing to the integration of ethnic groups and a heat of mixing to their tendency to segregate.⁵²

It is true that there is the danger of a lack of intellectual thoroughness in such extrapolations. Each one ought to be examined properly for mere shallow analogies.

Modern Version of Zeroth, First and Second Laws

Even though the historical development of thermodynamics makes interesting reading, it does not provide a full understanding of some of the subtleties in the field. Thus the early researchers invariably do not make it clear that the heat dQ and the work dW are applied to the *surface* of the body. Nor do they state clearly that the T and the p occurring in their equations, or inequalities, are the homogeneous temperature and the homogeneous pressure on the surface which may or may not be equal to those in the interior of the body; they *are* equal in equilibrium or in reversible processes, i.e. slow processes, but not otherwise.

The kinetic energy of the flow field inside the body is never mentioned by either Carnot or Clausius although, of course, its conversion into heat was paramount in the minds of Mayer, Joule and Helmholtz.

All this had to be cleaned up and incorporated into a systematic theory. That was a somewhat thankless task, taken on by scientists like Duhem, and

⁵⁰ According to S.G. Brush: “The Temperature of History. Phases of Science and Culture in the Nineteenth century.” Burt Franklin & Co. New York (1978).

⁵¹ N. Georgescu-Roegen: “The Entropy Law and the Economic Process.” Harvard University Press, Cambridge, Mass (1971).

⁵² I. Müller, W. Weiss: “Entropy and Energy – A Universal Competition, Chap. 20: Socio-thermodynamics.” Springer, Heidelberg, (2005).

A simplified version of socio-thermodynamics is presented at the end of Chap. 5.

Jaumann⁵³ and Lohr.^{54,55} These people recognized the first and second laws for what they are: Balance equations, or conservation laws on a par – formally – with the balance equations of mass and momentum.

Generically an equation of balance for some quantity $\Psi = \int_V \rho \psi dV$ in a volume V , whose surface ∂V – with the outer normal n_i – moves with the velocity u_i , has the form

$$\frac{d}{dt} \int_V \rho \psi dV = - \int_{\partial V} (\rho \psi (v_i - u_i) + \Phi_i) n_i dA + \int_V \sigma dV.$$

ρ is the mass density and ψ is the specific value of Ψ , such that $\rho \psi$ is the density of Ψ .⁵⁶ The velocity of the body, a fluid (say), is v_i . In the surface integral, $\rho \psi (v_i - u_i) n_i$ is the convective flux of Ψ through the surface element dA and $\Phi_i n_i$ is the non-convective flux. σ is the source density of Ψ ; it vanishes for conservation laws.

For mass, momentum, energy, and entropy the generic quantities in the equation of balance have values that may be read off from Table 3.1.

t_{ii} is called the stress tensor, whose leading term is the pressure $-p \delta_{ii}$; that is the *only* term in t_{ii} , if viscous stresses are ignored. E_{kin} is the kinetic energy of the flow field and q_i is the heat flux. Mass, momentum and energy are conserved, so that their source-densities vanish.⁵⁷ Note that the internal energy is not conserved, because it may be converted into kinetic energy. The entropy source is assumed non-negative which represents the growth property of entropy.

⁵³ G. Jaumann: “Geschlossenes System physikalischer und chemischer Differentialgesetze” [Closed system of physical and chemical differential laws] Sitzungsbericht Akademie der Wissenschaften Wien, 12 (IIa) (1911).

⁵⁴ E. Lohr: “Entropie und geschlossenes Gleichungssystem” [Entropy and closed system] Denkschrift der Akademie der Wissenschaften, 93 (1926).

⁵⁵ While Lohr is largely forgotten, Gustav Jaumann (1863–1924) lives on in the memory of mechanicians as the author of the *Jaumann derivative*, a “co-rotational” time derivative, i.e. the rate of change of some quantity – like density or velocity – as seen by an observer locally moving and rotating with the body; that derivative plays an important role in rheology and in theories of plasticity. Jaumann was a student of Ernst Mach and carried Mach’s prejudice against atoms far into the 20th century, thus making himself an outsider of any serious scientific circle. He died in a mountaineering accident.

⁵⁶ It has become customary in thermodynamics to denote global quantities – those referring to the whole body – by capital letters, and specific quantities – referred to the mass – by the corresponding minuscules.

⁵⁷ We ignore gravitation and radiation. See, however, Chap. 7, where radiation is treated. Gravitation changes thermodynamic in some subtle and, indeed, interesting ways, since the pressure field cannot be homogeneous in equilibrium, – neither on ∂V , nor in V . However, here is not the place to treat gravitational effects, because we do not wish to encumber our arguments. Let it suffice to say that in gases and vapours the gravitational effects are usually so small as to be negligible.

Table 3.1. Canonical notation for specific values of mass, momentum, energy and entropy and their fluxes and sources

Ψ	ψ	Φ_i	Σ
mass m	1	0	0
momentum P_l	v_l	$-t_{li}$	0
energy $U + E_{kin}$	$u + \frac{1}{2} v^2$	$-t_{li} v_l + q_i$	0
internal energy U	u	q_i	$t_{li} \frac{\partial v_l}{\partial x_i}$
entropy S	s	$\frac{q_i}{T}$ ⁵⁸	$\sigma \geq 0$

In order to clarify the special status of Clausius's first law, the equation for dU , we first observe that viscous forces did not enter Clausius's mind in connection with the first law. Also he considered *closed systems*, whose surfaces move with the velocity of the body on the surface so that no convective flux appears. Therefore Clausius would have written the equation of balance of energy in the form

$$\frac{d(U + E_{kin})}{dt} = \dot{Q} + \dot{W}, \text{ where}$$

$$\dot{Q} = - \int_{\partial V} q_i n_i dA \text{ is the heating, and}$$

$$\dot{W} = - \int_{\partial V} p v_i n_i dA \text{ is the working of pressure.}$$

The balance of internal energy should then have the form

$$\frac{dU}{dt} = \dot{Q} + \dot{W}_{int} \text{ where } \dot{W}_{int} = - \int_V p \frac{\partial v_l}{\partial x_l} dV \text{ is the internal working.}$$

If we assume that the pressure is homogeneous on ∂V , the first equation becomes⁵⁹

⁵⁸ This form of the entropy flux is nearly universally accepted, although the kinetic theory of gases furnishes a different form; the difference is small and we ignore it for the time being. See, however, Chap. 4.

⁵⁹ Note that $\int_{\partial V} v_l n_l dA = \int_V \frac{\partial v_l}{\partial x_l} dV = \frac{dV}{dt}$.

$$\frac{d(U + E_{kin})}{dt} = \dot{Q} - p \frac{dV}{dt};$$

and if we assume that the pressure is homogeneous throughout V , the second equation becomes

$$\frac{dU}{dt} = \dot{Q} - p \frac{dV}{dt}.$$

By comparison it follows that, for a homogeneous pressure p in V , there is no change of kinetic energy of the flow field which, of course, is reasonable. Indeed, according to the momentum balance, there is no acceleration in this case. Thus now, under all these restrictive assumptions – and with $\dot{Q}dt = dQ$ – we have obtained the Clausius form of the first law.

All these assumptions were *tacitly* made by Clausius, and his forerunners, and the majority of his followers to this very day. Indeed, among students thermodynamics has acquired the reputation of a difficult subject just *because* of the many tacit assumptions. The difficulty is not inherent in the field, however; it is due to sloppy teaching.

According to Table 3.1, the entropy balance contains a non-negative source density and a non-convective flux which is assumed to be given by q_i/T , so that we may write

$$\frac{dS}{dt} + \int_{\partial V} \frac{q_i n_i}{T} dA \geq 0.$$

This inequality is known as the *Clausius-Duhem inequality*. If T is homogeneous on ∂V , we may write

$$\frac{dS}{dt} - \frac{\dot{Q}}{T} \geq 0, \quad \text{where} \quad \dot{Q} = - \int_{\partial V} q_i n_i dA$$

and that is – again with $\dot{Q}dt = dQ$ – the form obtained by Clausius. He considered *only* this case. If T is not homogeneous on ∂V , the natural extension of his inequality was conceived by Pierre Maurice Marie Duhem (1861–1916).

Duhem was professor of theoretical physics in Bordeaux. He worked successfully in thermodynamics at the time when Gibbs was still unknown in Europe. However, he is also known as a philosopher of science, who expressed the view that the laws of physics are but symbolic constructions, neither true nor wrong representations of reality. He advocated metaphysical hypotheses for a provisional understanding of

nature. Somehow Duhem's ideas found their way from Bordeaux to Vienna, where they were welcomed by Ernst Mach who thought that science should concentrate exclusively on finding relations between observed phenomena, see Chap. 4. Duhem's thoughts helped to underpin this kind of positivistic thinking in what became known as the *Vienna circle*, a niche for philosophers belly-aching about truth in the laws of natural science. A latter-day representative of the school was Karl Raimund Popper (1902–1994) – Sir Karl since 1964 – in whose writings the dilemma is largely reduced to the question of how, or whether, and why we know that the sun will rise tomorrow, *after approximately 90,000 pulse beats*, – or will it everywhere and always? Popper wrote a book about this important problem.⁶⁰

The energy balance implies that the normal component of the heat flux q_i is continuous at a diathermic wall, i.e. a wall permeable to heat. The Clausius-Duhem inequality on the other hand implies that the normal component of $\frac{q_i}{T}$ is also continuous, provided that no entropy is produced in the wall. Therefore T must also be continuous. In this manner the zeroth law, cf. Chap. 1, may be said to represent a corollary of the Clausius-Duhem inequality. Its continuity is the defining property of temperature, and by virtue of the continuity, the temperature is measurable by contact thermometers. That is the reason why temperature plays a privileged role among thermodynamic variables. We shall review this role of temperature in Chap. 8, cf. Insert 8.3.

What is Entropy?

A physicist likes to be able to grasp his concepts plausibly and on an intuitive level. In that respect, however, the entropy – for all its proven and recognized importance – is a disappointment. The formula $dS = \frac{dQ}{T}$ does not lend itself to a suggestive interpretation.

What is needed for the modern student of physics, is an interpretation in terms of atoms and molecules. Like with temperature: It is all very well to explain that temperature is defined by its continuity at a diathermic wall, but the “ahaa”-experience comes only after it is clear that temperature measures the mean kinetic energy of the molecules, – and then it comes immediately.

Such a molecular interpretation of entropy was missing in the work of Clausius. It arrived, however, with Boltzmann, although one must admit, that the interpretation of entropy was considerable more subtle than that of temperature. Let us consider this in the next chapter.

⁶⁰ K.R. Popper: “Objective knowledge – an evolutionary approach.” Clarendon Press, Oxford (1972).